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Some Aspects of Mechanism for Stereospecific Polymerization

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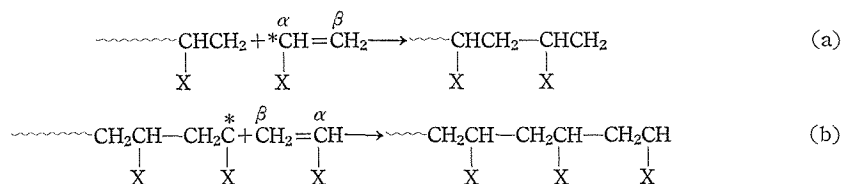
To discuss the mechanism for stereospecific polymerization it seems convenient to classify the reactions into two groups, i. e. homogeneous and heterogeneous systems. In the former case due to the steric hindrance between the substituent of polymer end and that of the penultimate unit, trans conformation is usually most favorable and syndiotactic polymer results and isotactic configuration will be possible if cyclic complex is formed between functional group at polymer end and that at penultimate unit. In the latter heterogeneous case isotactic polymers are afforded in most cases and the fact will probably be attributable to the steric hindrance between the substituent of monomer and the of polymer, where the end of polymer and the penultimate unit form cyclic intermediate complex with the functional atom on catalytic surface.

INTRODUCTION

Since the brilliant work of Natta, the study on the stereoregular polymerization has held one of the most important positions in polymer chemistry. A great deal of crystalline polymers was already prepared successfully not only of α -olefins or diolefins but also of vinyl, oxyran or carbonyl compounds. As to the mechanism for stereospecific polymerization many proposals or reviews have been presented, but it seems to be important to find out the correlation lying under several mechanisms and to determine their scopes for application. In other words, all discussions on this problem must be done according to the reaction condition, e, g., whether the reaction proceeds in homogeneous or heterogeneous system and whether by radical or ionic mechanism. This review deals with the problems concerning reaction mechanism for stereoregular polymerization based on the author's opinion.

I. TYPES OF REACTION AND MODES OF MECHANISM

The configuration of polymer is affected by the mode of mechanism for the chain growing step, which may be classified into the following two types.



They differ each other in the position of monomer to be attacked. In type (a)

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α -carbon of monomer is attacked, which controls the configuration of polymer.

While in type (b) the key atom (labelled with*) does not lie in monomer but in the terminal carbon of polymer chain, whose configuration is not yet settled before it combines with monomer. In other words in type (a) the configuration of polymer will be determined by the steric relation between two substituents, one belongs to polymer and the other to monomer, whereas in type (b) the configuration depends on two substituents, both of them lie on the polymer, one is on the terminal carbon and the other on the penultimate unit of polymer. Even in the latter case there may be the alternate concept that the interaction between the substituent of polymer terminal and that of α -carbon of monomer is also influential for determining the configuration of polymer. However the latter interaction may be not so influential, because the substituent of the terminal unit of polymer is not so close to that of the attacking monomer as to that of the penultimate unit of polymer.

The type of reaction varies with the polar nature of monomers or electronic type of reaction i. e. radical, anionic or cationic. In radical and cationic polymerizations, growing polymer end attacks always non-substituted carbon atom of monomer, while in anionic polymerization polymer end attacks the substituted carbon atom of negative monomer such as α -olefin, but it attacks non-substituted one of positive monomer such as acrylic compounds.

Table 1. Position in monomer to be attacked.

| Monomers | Radical | Cationic | Anionic |
|---|---|---|---|
| Negative monomers | | | |
| $\begin{matrix} \delta^- & \delta^+ \\ \text{CH}_2 & = \text{CHR} \end{matrix}$ | \downarrow $\text{CH}_2 = \text{CHR}$ | \downarrow $\text{CH}_2 = \text{CHR}$ | $\text{CH}_2 = \downarrow \text{CHR}$ |
| $\begin{matrix} \delta^- & \delta^+ \\ \text{CH}_2 = & \text{C} \begin{matrix} \nearrow \text{R} \\ \searrow \text{R}' \end{matrix} \end{matrix}$ | Not polymerized | \downarrow $\text{CH}_2 = \text{CRR}'$ | Not polymerized |
| $\begin{matrix} \delta^- & \delta^+ \\ \text{CH}_2 = & \text{CHOR} \end{matrix}$ | \downarrow $\text{CH}_2 = \text{CHOR}$ | \downarrow $\text{CH}_2 = \text{CHOR}$ | Not polymerized |
| Neutral monomers | | | |
| $\text{CH}_2 = \text{CHX}$ | \downarrow $\text{CH}_2 = \text{CHX}$ | Not polymerized | ? |
| Positive monomers | | | |
| $\begin{matrix} \delta^+ & \delta^- \\ \text{CH}_2 = & \text{CHCOOR} \end{matrix}$ | \downarrow $\text{CH}_2 = \text{CHCOOR}$ | Not polymerized | \downarrow $\text{CH}_2 = \text{CHCOOR}$ |
| $\begin{matrix} \delta^+ & \delta^- \\ \text{CH}_2 = & \text{CHCN} \end{matrix}$ | \downarrow $\text{CH}_2 = \text{CHCN}$ | Not polymerized | \downarrow $\text{CH}_2 = \text{CHCN}$ |

where R, R' = alkyl, aryl; X = halogen, RCOO.

In Table 1 the arrow indicates the position to be attacked in monomer. It is valuable to discuss the mechanism in terms of the mode (b) except for the case of anionic or strictly speaking co-ordinated anionic polymerization of α -olefins, since the latter is the only case of the mode (a).

II. THE HOMOGENEOUS POLYMERIZATION

As mentioned above the homogeneous polymerization, regardless of radical or ionic, proceeds through the mechanism of the type (b) and the conformation of terminal carbon in the transition state is the influential factor in deciding the final structure of polymer. Furukawa¹⁾ postulated the planar configuration and Cram²⁾, Coleman³⁾ and Fordham⁴⁾ the tetrahedral one for the structure of polymer end. In the former case two planes, one of which involves the substituents of the terminal carbon and the other involves the substituent of the third carbon from the terminal, may probably be perpendicular to the plane on which the zigzag main chain is lying and two bulky substituents may be occupied in mutually trans position due to steric hindrance or electrostatic interaction and if so, the configuration of the terminal carbon may be settled depending on the direction of attacking monomer as shown in Fig. 1. The attack from the lower side may probably be more favourable and the syndiotactic polymer will be afforded.

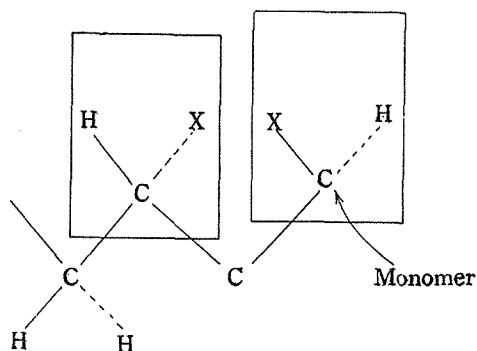


Fig. 1.

In the model proposed by Cram and others the mutual positions of two substituents and the attacking monomer are deciding factors. The Fordham's calculation⁵⁾ of electrostatic repulsion energy for vinylchloride polymerization indicated the trans conformation with respect to two halogen atoms, in which one is on terminal carbon and the other is on the third carbon, was the most probable one and preference of the syndiotactic structure was also concluded.

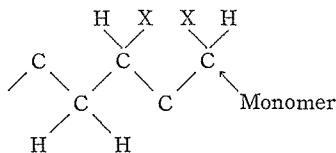
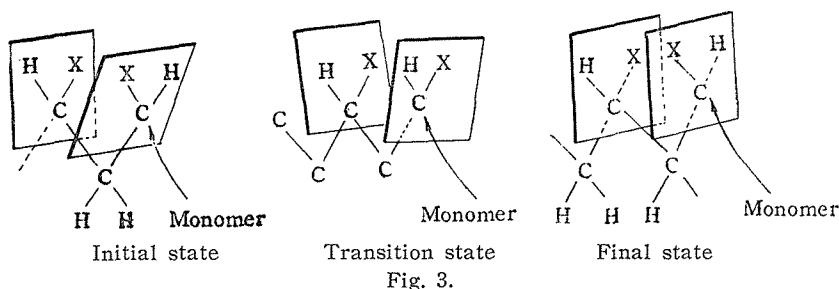


Fig. 2.

Both the planar model and tetrahedral one afford the same conclusion, despite of different conformations of transition state. In the planar model the transition state is rather similar to that in the initial state, whereas in the tetrahedral

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model to the final state. The actual structure in the transition state must lie between two states as illustrated in Fig. 3.

In conclusion it can be said however that there should not be the essential difference between them.

III. FACTORS AFFECTING THE STEREOREGULARITY IN THE HOMOGENEOUS POLYMERIZATION

From foregoing discussion the followings may be considered as the influential factors which affect the stereoregularity.

1. The Polymerization Temperature

According to T. G. Fox *et al.*⁶⁾ and J. W. L. Fordham⁴⁾ the ratio of rate constants for isotactic growing and syndiotactic one, k_i/k_s can be expressed as follows :

$$\frac{k_i}{k_s} = \exp\left(\frac{S_i^* - S_s^*}{R}\right) \exp\left(-\frac{H_i^* - H_s^*}{RT}\right)$$

where subscripts *i* and *s* imply isotactic and syndiotactic, respectively, *H* and *S* mean activation heat and entropy respectively. Fordham pointed out the important effect of the activation heat, which depends much on the electrostatic interaction between polar substituent groups. Fox *et al.*⁶⁾ has already calculated the temperature coefficient of stereoregularity and has shown that the regularity reaches to at 93% at -73°C when energy difference is 1 Kcal or 2 Kcals, whereas at 0°C it is 86% or 76%, respectively. A number of syndiotactic polymers was prepared successfully in the cases of vinylchloride⁷⁾ and methyl methacrylate⁸⁾, which were all made by the radical polymerization at low temperature of Dry Ice.

2. The Effect of Polar nature and Bulkiness of Substituent Group

The most influential factor for the stereoregularity is of course the interaction between two substituents, which is classified into two types *i. e.* electrostatic and steric hindrance. Fordham⁵⁾ emphasized the former effect in the experiments for radical polymerizations of vinyl chloride and of vinyl halogenoacetate, more syndiotactic polymer is obtained at lower temperature regardless of types of radical initiator. Regularity of polyvinyl halogenoacetates increases with increasing number of electronegative chlorine groups and trifluoroacetate

affords the most crystalline polymer. Acrylic ester gives also crystalline polymer in the case of tertiary butyl acrylate⁹⁾ and this fact indicates the importance of steric hindrance of bulky tertiary alkoxy group.

3. The Effect of Counter Ion and Solvent

Preparation of isotactic polymer of methacrylic ester was succeeded by research group of Rohm and Haas Corp.¹⁰⁾ using butyllithium as catalyst in non polar solvent. Phenylmagnesium bromide¹¹⁾ and calcium zinctetraethyl¹²⁾ were also found to be suitable catalyst. The latter two catalysts afforded crystalline polymers even at room temperature. It is important that the addition of polar solvent tends to lose the counter ion effect and the syndiotactic polymer is produced in the solution polymerization of methacrylate in dimethoxyether of ethylene glycol catalyzed by alkyllithium. Recently D. J. Cram *et al.*¹³⁾ proposed a complex ion model for isotactic polymerization in non polar solvent, where the enolated end of growing polymer forms a chelate ring with carbonyl group of the penultimate unit as illustrated in Fig. 4.

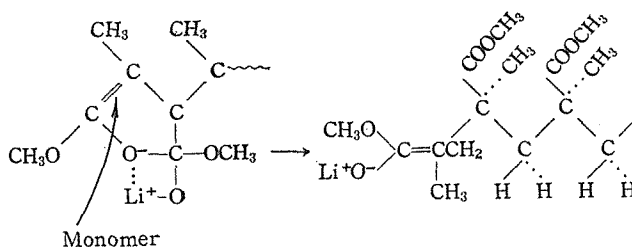


Fig. 4.

The divalent nature of lithium ion had already been postulated by R. S. Stearns and L. E. Forman¹⁴⁾ in the interpretation of the cis-1,4 polymerization of isoprene as is shown in Fig. 5, where divalent lithium atom forms stable six-membered ring with isoprene molecule and terminal atom of the polymer.

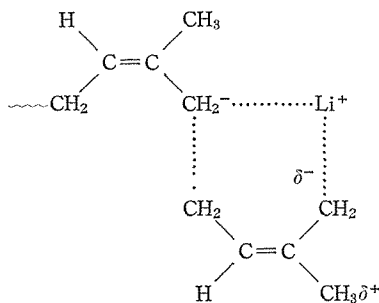


Fig. 5.

In the model indicated in Fig. 6, where the lower side is occupied by counter ion and the attacking monomer should be located in the opposite upper side. Thus isotactic polymer may result unlike radical reaction. The isotactic polymerization of vinyl ether catalyzed by boron trifluoride found by Schildknecht

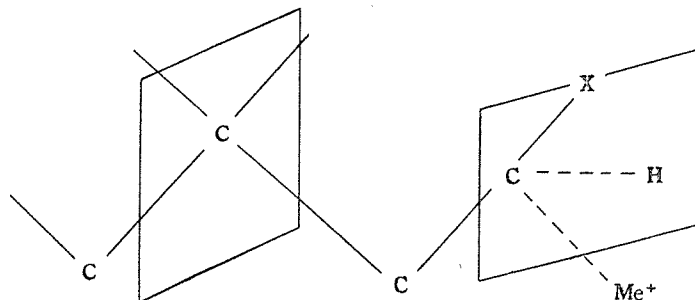


Fig. 6.

will be also similarly accounted for by the counter anion effect.

Stereospecific nature of Grignard reagent and calcium zinctetralkyl is however to be interpreted by the heterogeneous catalytic system as mentioned later.

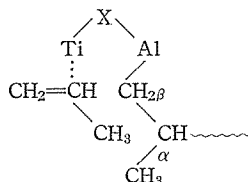
Generally speaking, counter ion may play great role as far as the catalyst is used in non-polar solvent, otherwise the ion pair in polymer end may be dissociated and the effect of counter ion will disappear. Tobolsky¹⁵⁾ has pointed out the solvent effect in cis-1, 4 polymerization of isoprene catalyzed by alkyl lithium, where the decrease in cis-1, 4 content by using polar solvent such as ether or amine was remarkable and alkylsodium instead of alkyl lithium afforded 3, 4-polymer because of the loss of the specific nature advantage for ion pair of metal alkyls.

From these points of view the non-polar solvent is proposed to be favorable to stereospecific polymerization. Recently, however, Burleigh¹⁶⁾ has found that aldehydes are effective additives for syndiotactic polymerization of vinyl chloride, although the mechanism is not clear. The complex formation of polymer terminal with aldehyde will possibly be supposed.

IV. THE HETEROGENEOUS POLYMERIZATION

Isotactic polymerization of α -olefins by the Ziegler-Natta catalyst is still interesting from the view-points of industrial and scientific application. The problem, whether the polymerization takes place on the surface of catalyst as Natta's proposal or it does in homogeneous system, is not yet completely settled. In fact, several soluble catalysts such as the complex derived from di- or tri-cyclopentadienyltitanium chloride was proposed for polymerization, but little was known as to the stereoregularity of α -olefin other than ethylene polymer prepared by the above catalyst. Natta asserted that the most excellent stereoregular poly- α -olefin is prepared only by the heterogeneous catalyst consisting of titanium trichloride and organo-beryllium or aluminum and if so, the stereospecificity should be attributed to the stereospecific residual valence, by which monomer or polymer end is favorably coordinated to catalyst surface as was named "Coordinated Polymerization" by him. Natta¹⁷⁾ made clear the structure of the Ziegler type catalyst consisting of cyclopentadienyltitanium dichloride and triethylaluminum to be a complex each components of which are combined by electron deficient bond or half bond of aluminum and titanium, such as

$(C_6H_5)_2Ti \begin{smallmatrix} \diagup Cl \\ \diagdown Cl \end{smallmatrix} Al(C_2H_5)_2$. Patat¹⁸⁾ and Furukawa¹⁹⁾ proposed the mechanism for co-ordinated polymerization in terms of such half-bonded complex as this. In both cases it is necessary to restrict the free rotation of bond of polymer end in order to fix spatially the substituent on α -carbon atom in polymer. Patat claimed that such restriction may be expectable from the character of complex, but it seems doubtful if the rotation of bond between C (α) and C (β) is affected by the nature of Ti-Al complex.



Furukawa's hypothesis is favorable for interpreting the restriction of the free rotation, in which hydrogen atom attached to α -carbon forms hydride bond with aluminum atom. The facility of hydride ion transfer to aluminum or to other monomer will support such a pseudo-hydride bond as shown in Fig. 7.

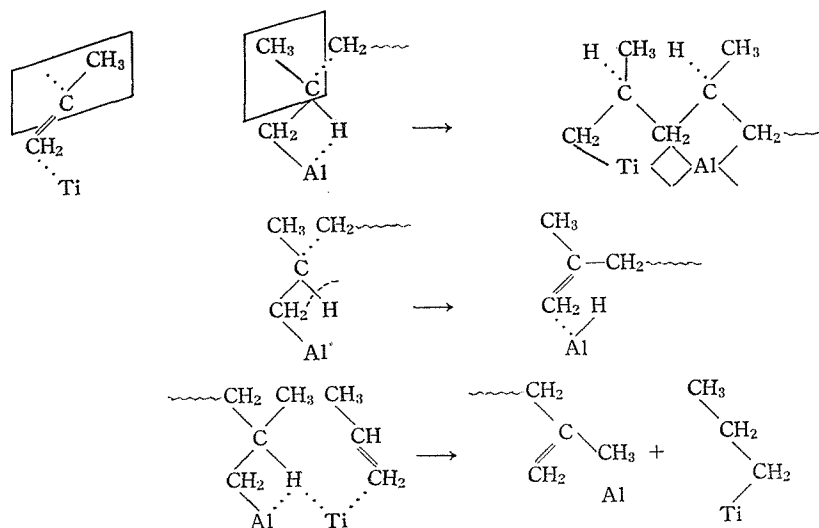


Fig. 7.

Stereospecificity may be attributable to the steric hindrance between each methyl group, which will probably diminish in trans conformation. From this consideration the isotactic polymer is preferred. The detail is illustrated by Fig. 8.

There is another question as to the real active species responsible for growing step, aluminum or titanium. Nenitzescu²⁰⁾ and others found the similar activity of titanium chloride promoted with sodium alkyls instead of aluminum alkyl and Du Pont²¹⁾ claimed the titanium compounds of two or three valence state were all active irrespective of kinds of metalalkyl and even metal itself such as zinc was also useful as a promoter. Ludlum²²⁾ stated the metalalkyl

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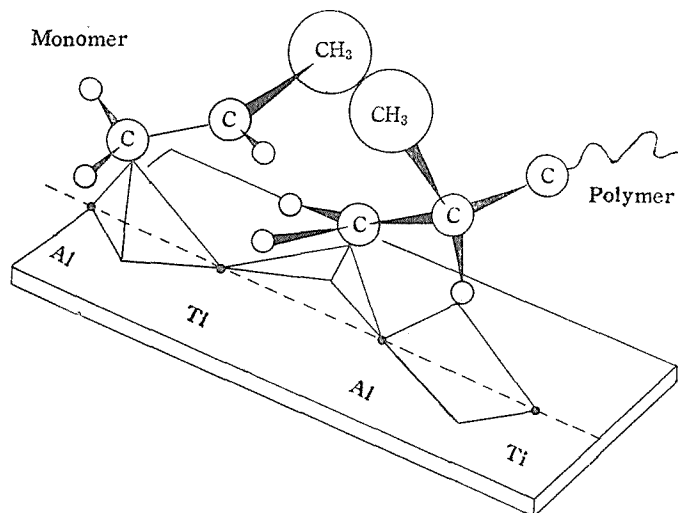


Fig. 8.

acted merely as reducing or alkylating agent of titanium compounds and alkylated compound of low valent titanium is the real active species²³⁾. Natta²⁴⁾ clarified that chain polymerization started from aluminum atom by the experiment with triphenylaluminum, where the polymer obtained contains phenyl group as the terminal end of polymer chain, whereas no phenyl group was detectable in case of phenylated titanium compounds used with triethylaluminum. But he did not make it clear which is responsible for growing reaction, aluminum or titanium. Recently W. L. Carrick *et al*²⁵⁾ has pointed out that propylene content in ethylene-propylene co-polymer was not affected by the kind of metalalkyl component such as triethylaluminum, diphenylzinc, di-*n*-butylzinc or methyltitanium trichloride but affected only by the Lewis acid component used *i. e.* chlorides of hafnium, zirconium, titanium or vanadium according to their electronegativities. He concluded that the catalyst did not involve any of metal alkyl components, the latter acted merely as reducing or alkylating agent for titanium compound and the complex of double components which is bonded by electron deficient bonding, as mentioned above, was not always necessary species. His interpretation seems to be favorable for the co-polymerization problem but not for the problem on stereoregularity, because the latter was much affected by the kind of metal alkyls, as stated by Natta previously, *i. e.* the metal having small ionic radius such as beryllium or aluminum afforded better regularity to polymer. This paradox may be settled by assuming that the growing reaction consists of two steps, *i. e.* firstly the chemisorption of monomer on the catalyst surface and secondly the electron transfer from polymer end to olefin, as shown in Fig. 7.

The overall reaction rate constant will be expressed by the product of chemisorption constant and electron transfer rate constant, where the former is reasonably assumed to depend mainly on the electronegativity of Lewis' acid component but not on the metalalkyl one and, on the contrary, in the latter process

the situation is reversed. The determining step for stereoregularity will be in the final chemical process, whereas the preferential adsorption of ethylene or propylene will be influenced by the acidity of Lewis' acid component

The stereoregular polymerization of polar vinyl monomers is mainly carried out in homogeneous system but it has been possible also in heterogeneous one by using the modified Ziegler catalyst, especially together with the modifying agent such as cyclic ether or amine in order to regulate activity of catalyst, otherwise the catalyst tends to add on carbonyl unsaturation of acrylic compound to give other by products. Some patents claimed the use of Ziegler type catalyst consisting of vanadium, titanium halides together with metal alkyls in the presence of modifying agent to prepare regular polymer of acrylic ester, vinyl chloride or vinyl acetate. Crystalline polymethyl methacrylate was also prepared successfully by calcium zinctetraethyl. All these method may be interpreted in terms of the mechanism like that indicated above.

V THE POLYMERIZATION OF OXYRAN RING COMPOUNDS OR CARBONYL COMPOUNDS

The polymerization of alkylene oxide such as ethylene oxide or propylene oxide and that of aldehydes afford another interesting field in addition to vinyl polymerization, the former of which was pioneered by C. C. Price²⁶⁾ and the latter by our laboratory²⁷⁾.

As catalyst for polymerization of ethylene- and propylene oxide polymerization many catalysts were proposed such as metalalcoholates, metal oxides, metal-alkyls and metal halides, *i. e.*, in general they are Lewis' base and Lewis' acid. C. C. Price *et al.* recommended the complex of aluminum alkoxide and zinc or ferric chloride and Furukawa the complex of zinc alkyls combined with water or alumina. In all cases crystalline polypropylene oxide is formed partly. Price *et al.* proposed from the stereospecific point of view a mechanism involving an intermediate complex consisting of monomer, terminal end and catalyst component illustrated in Fig. 9.

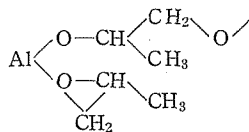


Fig 9.

He assumed the planar conformation as to the four atoms lying along the main chain of growing polymer end in order to interpret spatial hindrance between neighboring two methyl substituents, but in case of heterogeneous catalytic system the orientation of the polymer is possible more easily by assuming cyclic intermediate which is attached to catalyst in two sites of polymer as cited in Fig. 10.

Alumina itself has the catalytic ability, but if it is treated with a controlled amount of diethylzinc prior to use, polymer of high molecular weight is pro-

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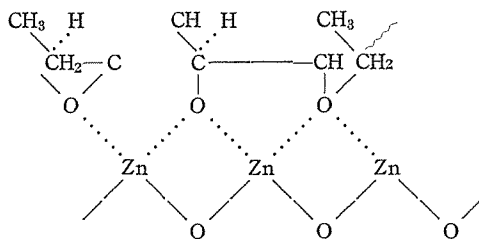


Fig. 10.

duced in much higher yield. In the former case basic hydroxyl group located on the catalyst surface acts as initiator but it acts also as proton doner and as terminator, because of amphoteric nature of aluminum hydroxyl.

When alumina is treated with diethylzinc the hydroxyl group is converted into ethylzinc-oxyl group, which exhibits the similar initiating ability but no terminating one. Diethylzinc treated with equivalent amount of water is also found to be another excellent catalyst, whose composition is known to be $R(ZnO)_x \cdot ZnOR$ ($x > 1$) from analytical data²⁸. It may have the similar structure as the former catalyst, where alkyl or alkoxy group attached to the back bone of zinc oxide will act as an initiator. Fig. 11 shows the hypothetical structure of both catalysts.

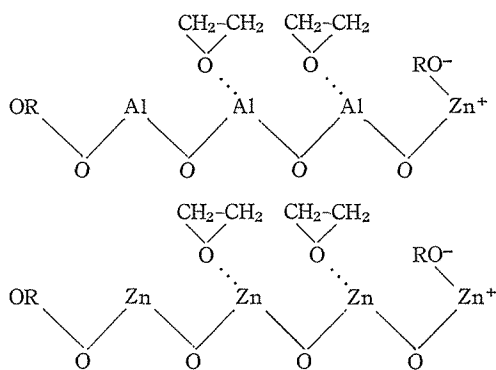
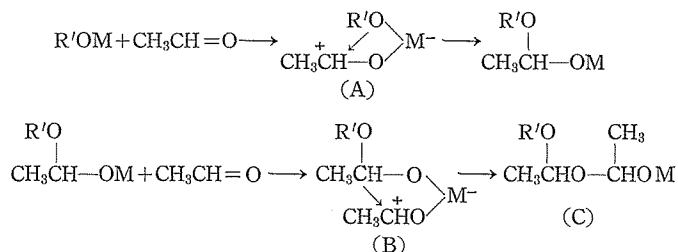


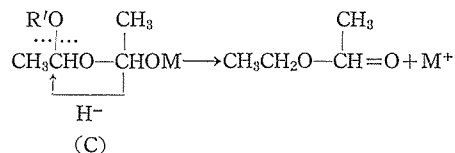
Fig. 11

Polyacetaldehyde of high molecular weight which is white rubber-like material has long been studied by Letort, who concluded that the polymerization took place on frozen acetaldehyde at extremely low temperature. The authors have found it was possible to polymerize in liquid state using gamma-alumina as catalyst at the temperature of Dry Ice and yield of high polymer was rather fair. The crystalline polymer has also been independently obtained by the author²⁹ and Natta³⁰ using organometallic compounds as catalyst at low temperature although the regularity depended on the kind of catalyst used such as ethyl or butyl compounds of lithium, zinc, cadmium, boron, aluminum and magnesium and the monomer applied such as acetaldehyde, propionaldehyde and chloral. Since usual metalalkyls tend to add to the carbonyl compounds at somewhat higher temperature than that at which the polymerization is carried out, the first step in polymerization may be the same as this and the actual

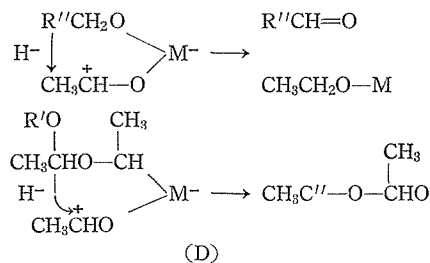
catalyst should be the metal alcoholate produced by the addition of metal alkyl to aldehyde. Indeed, other metal alkoxides have been known to have the polymerization activity, though activity is not the same as the corresponding metal alkyl.



At room temperature the main product is ethyl acetate, which is resulted from the intermediate alcoholate (C) by intramolecular hydride ion transfer as follows,



This reaction is known as Tischchenko's reaction. Such a hydride ion transfer is possible also in the intermediate complex (A), which is called as Meerwein complex, and (D), where intermolecular transfer causes wellknown Meerwein-Ponndorf reduction as follows :



In order to obtain high polymer it is important to prevent such a hydride ion transfer, and the low temperature might enable it. The stereoregularity of polyaldehydes will be attributed to the steric hindrance in the intermediate complex like Meerwein complex where it is so large enough to hold stereoregularity if the co-ordination with catalyst is assumed not only of oxygen atom of chain end but also of penultimate unit as shown in Fig. 12.

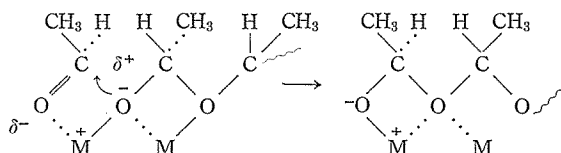


Fig. 12.

Some Aspects of Mechanism for Stereospecific Polymerization

The assumption is quite similar to that applied to the polymerization of α -olefin by Ziegler's catalyst and of propylene oxide by alumina or zinc oxide (cf. Fig. 7 and Fig. 10).

The polymerization of propylene oxide affords the least regularity in comparison with other two cases and this fact will probably be due to the unrigid structure of intermediate complex of polymer end, polypropylene oxide forms five-membered ring, whereas polypropylene and polyacetaldehyde do four-membered one.

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